

CLASSIFICATION **CONFIDENTIAL**  
 CENTRAL INTELLIGENCE AGENCY **CONFIDENTIAL** REPORT  
 INFORMATION FROM  
 FOREIGN DOCUMENTS OR RADIO BROADCASTS CD NO.

50X1-HUM

COUNTRY USSR  
 SUBJECT Scientific - Chemistry  
 HOW PUBLISHED Monthly periodical  
 WHERE PUBLISHED Moscow  
 DATE PUBLISHED Sep 1949  
 LANGUAGE Russian

DATE OF INFORMATION 1949  
 DATE DIST. 4 Apr 1950  
 NO. OF PAGES 3  
 SUPPLEMENT TO REPORT NO.

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SOURCE Izvestiya Akademii Nauk SSSR, Otdeleniye Tekhnicheskikh Nauk, No 9, 1949.

THE MECHANISM AND KINETICS OF OXIDATION  
 OF LEAD SULFIDE BY OXYGEN

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 Acad Sci USSR; Submitted 2 April 1949

[A digest]

Roasting sulfides to oxidize them is of great importance in the metallurgy of nonferrous metals. There is much published data on this subject (1) and furthermore, works devoted to the study of the kinetics and mechanism of oxidation of sulfides have been generalized in courses on metallurgy.(2)

There are two basic theories explaining the mechanism and kinetics of oxidation of sulfides. The first, the "sulfate" theory, claims that the process proceeds through an intermediate stage in which sulfates are formed. The sulfates are then decomposed to form oxides of the metals and sulfur. Depending on the temperature and the concentration of the sulfur anhydride and oxygen in the gaseous phase, these oxides can again be transformed into sulfates. Consequently, there arises the possibility that both primary and secondary sulfate formation may occur.

The other theory, the "oxide" theory, claims that the sulfides are oxidized directly into oxides, and that the sulfates are formed afterward by addition of the elements of sulfur trioxide to the oxides.

Many metallurgists favor a combination of these theories, namely that the primary products of the oxidation are both sulfates and oxides of the metals.

An argument supporting the sulfate theory is the fact that, as a result of oxidizing sulfides at comparatively low temperatures of from 100 to 600 degrees, sulfates are formed for the most part.(3)

- 1 -

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Therefore, even at present there is no generally accepted theory in regard to the mechanism and kinetics of this process. However, all authors agree on one point: in the interaction of metallic sulfides with oxygen, depending on the conditions of the reaction, it is possible to obtain a mixture of sulfates, oxides, and unreacted sulfide, as well as a gaseous phase consisting of sulfur oxides and oxygen.

The purpose of this investigation was to study the mechanism and kinetics of the oxidation of lead sulfide, i.e., to determine the nature and sequence of the basic chemical reactions taking place in the process. The investigation is divided into two parts: (1) thermodynamic calculations by means of which it was possible to determine the probability of these or other reactions and their direction in relation to changes in temperature, but which did not clarify either the mechanism of the reactions or the rate at which they proceeded, and (2) experimental research on the kinetics and mechanism of the oxidation of galena.

#### Conclusions

In this investigation, the following individual reactions were noted:

As a result of the interaction of lead sulfide with pure oxygen, the primary product of the oxidation is lead sulfate, according to the reaction  $PbS + 2O_2 = PbSO_4$ . The intensity of the reaction is determined by the concentration of oxygen in the gaseous phase and the temperature of the process. The greater the partial pressure of oxygen and the higher the temperature, the greater the rate of the reaction which forms the primary lead sulfate.

This sulfate may then interact with the unreacted sulfide according to the equation  $PbS + PbSO_4 = 2Pb + 2SO_2$ , at a rate which depends on the temperature and the concentration of the reacting substances. The metallic lead, in the presence of free oxygen, is then oxidized according to the equation  $2Pb + O_2 = 2PbO$ .

Therefore, the formation of lead oxide as a result of the oxidation of the sulfide with oxygen proceeds over the metallic phase.

However, the oxidation process is not limited to just these reactions. They are only the main ones. Many concomitant reactions occur, the mechanism of which has not yet been studied. For example, the lead oxide which is formed in the manner described can interact with the unreacted sulfide according to the reaction  $PbS + 2PbO = 3Pb + SO_2$ . The lead oxide with its sulfate forms basic sulfates.

The presence of three of these sulfates --  $PbO \cdot PbSO_4$ ,  $(PbO)_2 \cdot PbSO_4$ , and  $(PbO)_3 \cdot PbSO_4$  -- was detected; they also can react with the primary lead sulfide.

Further study of the individual reactions should lead to a more complete understanding of the mechanism of this process in its entirety.

Tabular results of the thermodynamic calculations and various experimental data

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- 2 -

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- 3 -

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